

The Biogeochemical Sulfur Cycle in the Marine Boundary Layer over the Northeast Pacific Ocean

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Abstract. The major components of the marine boundary layer biogeochemical sulfur cycle were measured simultaneously onshore and off the coast of Washington State, U.S.A. during May 1987. Seawater dimethylsulfide (DMS) concentrations on the continental shelf were strongly influenced by coastal upwelling. Concentration further offshore were typical of summer values (2.2 nmol/L) at this latitude. Although seawater DMS concentrations were high on the biologically productive continental shelf (2–12 nmol/L), this region had no measurable effect on atmospheric DMS concentrations. Atmospheric DMS concentrations (0.1–12 nmol/m³), however, were extremely dependent upon wind speed and boundary layer height. Although there appeared to be an appreciable input of non-sea-salt sulfate to the marine boundary layer from the free troposphere, the local flux of DMS from the ocean to the atmosphere was sufficient to balance the remainder of the sulfur budget.

Key words. Dimethylsulfide, sulfate, sulfur dioxide, methane sulfonate, biogeochemical sulfur cycle, air-sea exchange.

1. Introduction

Sulfate aerosol particles are a dominant component of the acid-base chemistry in the marine troposphere (Charlson and Rodhe, 1982; Galloway *et al.*, 1982) and are a major source of cloud condensation nuclei (CCN) (Dinger *et al.*, 1970; Twomey, 1971; Hobbs, 1971). In remote areas where the total particle population limits the CCN population (Elliott and Egami, 1975; Hoppel, 1979), the number of sulfate aerosol particles acting as CCN may affect the optical properties of clouds and thus influence the radiative climate of the Earth (Charlson *et*

al., 1987; Coakley *et al.*, 1987). An understanding of the cycling of sulfur through the atmosphere, therefore, is important in order to assess the effect of anthropogenic and natural sulfur emissions on global climate change.

Over the oceans, biogenic dimethylsulfide (DMS) is a major source of sulfur to the troposphere (Andreae, 1986; Bates *et al.*, 1987). These biogenic sulfur emissions are thought to be a dominant precursor of sulfate aerosol particles in the remote marine troposphere (Bonsang *et al.*, 1980; Bigg *et al.*, 1984). The importance of DMS emissions to the marine tropospheric sulfur cycle, though, depends upon the relative magnitude of this source versus the transport of continental sulfur out over the oceans. By using simultaneous measurements of the key oceanic (DMS) and atmospheric (DMS, sulfur dioxide, and sulfate and methanesulfonate aerosol particles) species, it is possible to create a simple box model to determine if the oceanic flux of DMS to the atmosphere is sufficient to account for the concentration of the various oxidized atmospheric sulfur species. Andreae (1986) used this approach with average concentrations and found that the sulfur cycle in the tropical marine troposphere could be balanced solely by the emissions of oceanic DMS. Using a similar approach during a period of low DMS emissions over the Northeast Pacific Ocean, Andreae *et al.* (1988) were able to show the importance of long-range transport from distant continents on the sulfur cycle in the free troposphere. Berresheim (1987) measured the key oceanic and atmospheric species in the southern ocean and showed that the calculated flux of DMS to the atmosphere was more than sufficient to account for the concentrations of the oxidized atmospheric sulfur compounds.

In this paper, we report measurements of oceanic DMS and atmospheric DMS, sulfate and methanesulfonate (MSA) made aboard the research vessel McArthur off the coast of Washington State, U.S.A. along with simultaneous measurements of atmospheric DMS, sulfur dioxide, sulfate and MSA made at the University of Washington's Cheeka Peak Research Station located 3 km from shore at an elevation of 480 m above sea level (Figure 1). This study, conducted during 8–21 May 1987, was during a period of high oceanic DMS concentrations, especially in the biologically productive coastal upwelling region. The seawater data collected from the same area during 19–22 May 1983, 15 February 1984, 28 August 1984, 13–17 May 1985, 18–30 April 1986, and 11–14 June 1986 are presented for comparisons. The simultaneous shipboard and shore based measurements in 1987 permit an evaluation of the importance of the coastal and open ocean DMS emissions on the tropospheric biogeochemical sulfur cycle.

2. Methods

Seawater samples were collected from a depth of approximately 5 m using the ship's seawater pumping system and were immediately analyzed on board ship (Bates *et al.*, 1987). Aliquots of these samples were gently filtered through a 0.4

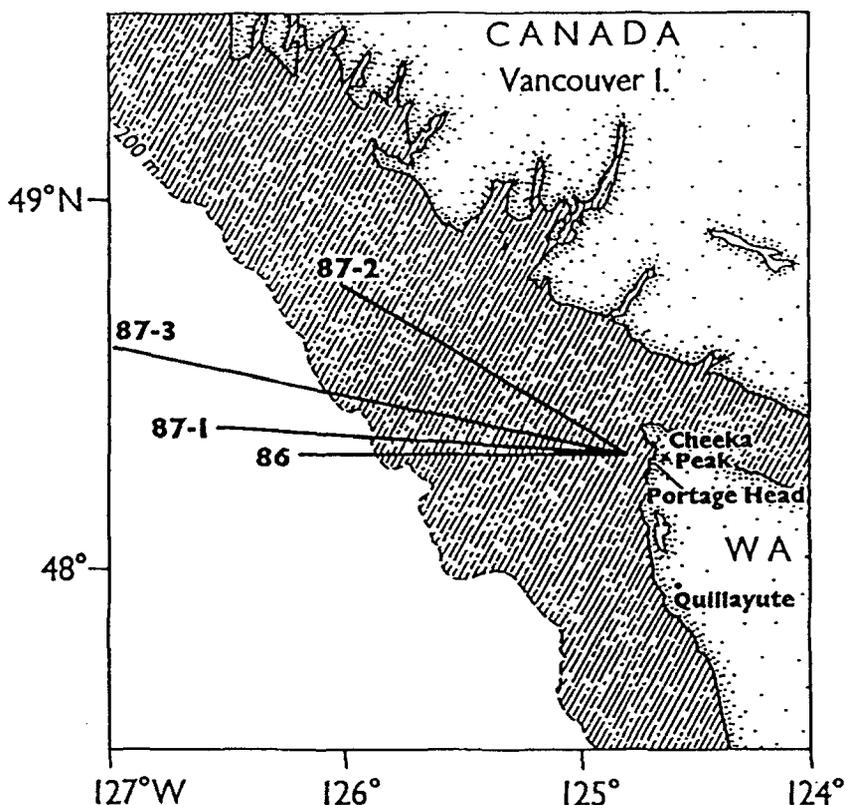


Fig. 1. Map of the study area along the coast of Washington State. The shaded region is the continental shelf defined by the 200 m depth contour. The ship transects are shown with the year (June 1986 and May 1987) and transect number. The shore based operations were on Cheeka Peak and on the beach immediately west of the peak.

μm Nuclepore filter and 2–10 ml of the sample were valved to a Teflon[®] gas stripper. The samples were purged with ultra-pure hydrogen at 60 ml/min for 5–20 min. The entire purge and trap system was made from Teflon with the exception of the Nitronic 60 Valco valves. Water vapor was selectively removed from the stripper gas stream in a Teflon loop held at -50°C while the sulfur gases were trapped in a narrow bore Teflon loop held at liquid argon temperature. After purging the water sample, the liquid argon trap was electrically heated and the volatile compounds were transferred to a DB-1 thick film ($5\ \mu\text{m}$) mega-bore fused silica column (J & W Scientific). The sulfur compounds were separated using a temperature program from 5 to 105°C and were quantified with a flame photometric detector. The flame was modified with the addition of approximately 60 ppb SF_6 to increase sensitivity and to provide a linear detection range from 0.15 to 15 pmol of sulfur (Goldan *et al.*, 1987). The detector itself was modified with a chimney over the jet to minimize flame (peak) broadening and enhance sensitivity (Barinaga and Farwell, 1986). The system was

calibrated using gravimetrically calibrated permeation tubes. The precision of the analysis, based on replicate analyses of a single water sample, was typically $\pm 10\%$. The performance of the system was monitored regularly by running blanks and standards through the entire system. Recovery of DMS from seawater was generally $>90\%$ while system blanks were below the detection limit. Values reported here have been corrected for recovery losses.

Air samples collected aboard ship were pulled through a KOH impregnated glass fiber filter (Goldan *et al.*, in prep.) to eliminate oxidant interferences (Andreae *et al.*, 1985; Berresheim, 1987), then through a Teflon loop at $-50\text{ }^{\circ}\text{C}$ to eliminate water vapor, and finally through a Teflon loop immersed in liquid argon to trap the DMS. The volume sampled (typically 1 liter) was determined by the pressure increase in a previously evacuated volume used to draw the sample. The trapped DMS was analyzed on the same system used for seawater DMS analysis. The performance of the analytical system was tested by adding a low loss (1.75 ng S/min) permeation tube in the upstream end of the approximately 70 m intake air line. The line was continuously flushed with an air flow of 6.0 L/min. Based on standard addition, the recovery was $96 \pm 4\%$. On shore, air samples were collected and analyzed with the NOAA/Aeronomy Laboratory sulfur system. The system, which has been previously described (Goldan *et al.*, 1987), was modified to include the KOH filters and water trap described above. The two systems and standards were intercalibrated at Cheeka Peak during April of 1987, and found to agree within the precision of the analysis (10%).

Aerosol particles and gaseous sulfur dioxide were collected with a stacked sampling system consisting of a cyclone separator (50% collection efficiency at $0.9\text{ }\mu\text{m}$ for NaCl particles at 85% relative humidity) followed by a $1.0\text{ }\mu\text{m}$ pore size Millipore Teflon particle filter and four 47 mm Whatman 41 filters coated with LiOH (Quinn and Bates, 1989). The particle filters have a $>99\%$ collection efficiency for particles with diameters $>0.035\text{ }\mu\text{m}$ (Liu and Lee, 1976). The laboratory recovery efficiency for SO_2 on the LiOH filters was $88 \pm 9\%$ with 99% of that collected on the first filter (Quinn and Bates, 1989). A second stacked filter pack (flow rate = 0 slpm) was mounted alongside each sample filter pack (flow rate = 50 slpm) to serve as a sampling and analytical blank. Aboard ship, the filter packs were mounted on a boom extending 6 m off the port forward quarter and 10 m above the sea surface. The air inlet to the DMS sampling system was located at the end of this boom. Sampling was conducted only when the wind was off the port bow and only during periods of SW to NW on-shore winds. During these periods, the ship made slow transects (3 knots) starting at the coast and heading off-shore (Figure 1). On Cheeka Peak, the filter packs were mounted on top of the sampling tower, approximately 7 m above the ground. The filters were changed in a SO_2 free glove box to minimize contamination and the filter packs were sealed in plastic bags during transport between the laboratory and sampling boom/tower. The particle filter was extracted with 1.0 ml of CH_3OH and 9.0 ml of water and the Whatman filters were extracted with 10 ml

of 0.1% H_2O_2 to convert all sulfur (IV) to sulfate. The extracts were analyzed by ion chromatography using AS-4 and CS-1 Dionex columns. The Na^+ concentration was used to calculate the amount of sea-salt sulfate which was always less than 8% of the total sulfate. The remaining sulfate is referred to here as non-sea-salt (NSS) sulfate. Since the cyclone separator eliminated most of the particles with diameters $>0.9 \mu\text{m}$, the NSS SO_4^{2-} and MSA concentrations reported here include mainly the sub- μm fraction. The average particulate SO_4^{2-} and gas-phase SO_2 blank concentrations were $<1\%$ and $4.9 \pm 2.5\%$ of the sample, respectively. All concentrations are reported in nmoles/m^3 at standard temperature (25°C) and pressure (101.3 kPa) such that 1 nmol/m^3 corresponds to a mixing ratio of 24.5 ppt(v). All times are reported in local daylight savings time which was seven hours behind UCT.

Continuous measurements were made of surface seawater chlorophyll 'a' concentrations (Lorenzen, 1966), pH (Fuhrmann and Zirino, 1988), nitrate (Parsons *et al.*, 1984) and temperature along with atmospheric temperature, humidity, and total particle concentration (diameters $>0.01 \mu\text{m}$) as measured with a TSI condensation nuclei counter.

3. Meteorological Conditions and Air Mass Trajectories

Upper air wind, temperature, and humidity data were available twice per day from the National Weather Service's Quillayute Station located 30 km SSE of Cheeka Peak and from occasional radiosondes launched from the ship or beach below Cheeka Peak. The weather patterns during this period began with surface high pressure to the northwest, contributing to northerly flow at the location of the ship from 8–10 May.

Southerly flow preceded the frontal passages on 11 and 14 May and was followed by westerly flow in the high pressure behind the fronts on 12 May and 14–15 May. With high pressure to the west and low pressure to the northwest, the flow remained westerly on 16–17 May. As the low center moved inland, a trough formed over the Great Basin contributing to northerly flow from 18–21 May. The weather was generally cloudy or partly cloudy with significant precipitation only during the frontal passages.

The marine boundary-layer height was defined as the point where the air temperature began to increase and the dew point sharply decreased. We use the term 'mixed layer' and 'boundary layer' interchangeably and consider this to be the layer from the ocean surface to the top of the lowest cloud layer. During the sampling period, the boundary-layer height varied from 0.2 to 2.1 km (Figure 2). The boundary layer could not be defined in this manner during the frontal passages on the afternoon of 11 May and the morning of 14 May.

Four day isentropic air mass back trajectories were calculated for the period of 13–20 May (Figure 3) using the isentropic trajectory model of Haagensen and Shapiro (1979). The trajectories shown were computed on isentropic surfaces

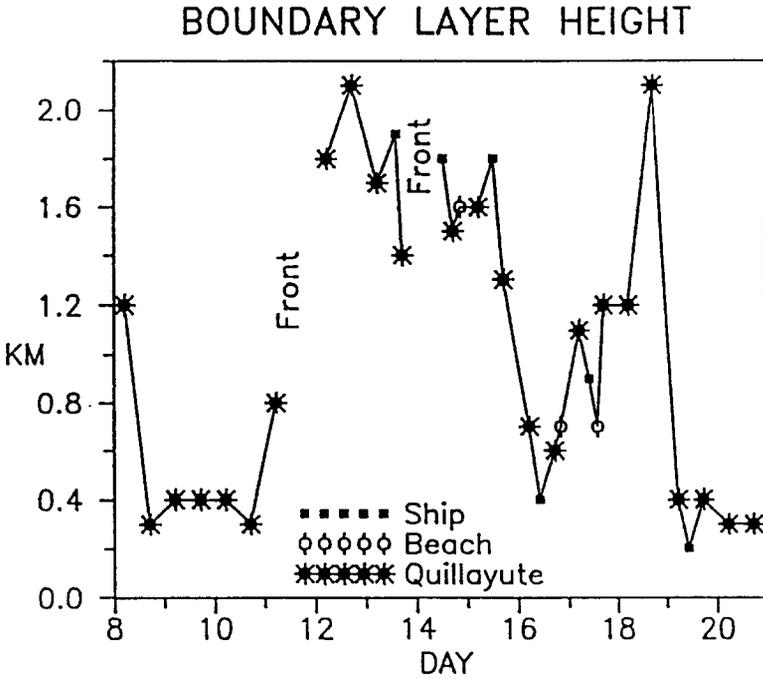


Fig. 2. Boundary layer height during 8–21 May, 1987. The radiosonde data were collected from the National Weather Service’s Quillayute station, the NOAA ship McArthur, and the beach immediately west of Cheeka Peak. There was no definable boundary layer height during the passage of the two fronts.

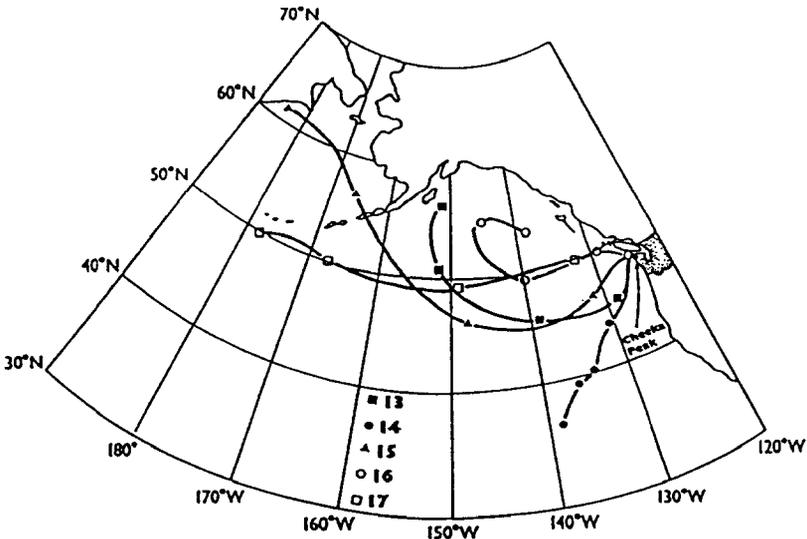


Fig. 3. Isentropic four day back-trajectories for 13–17 May 1987 at 1700 local time (0000 UCT). The symbols are at 24 hour intervals. The potential temperatures are shown in Figure 4.

that intersected the latitude and longitude of Cheeka Peak at about 600–800 m above sea level. The points shown on Figure 3 are those calculated at 1700 each day. The potential temperatures of the surfaces ranged from 285–288 °K. Trajectories were computed on other surfaces as well in order to determine the sensitivity of the trajectory computation to height. With the exception of 14 May, a period immediately following a frontal passage, the trajectories show subsidence near the coast (Figure 4), similar to the sampling conditions experienced in 1985 (Andreae *et al.*, 1988). Upper level trajectories for 14 May, however, did show substantial subsidence and had origins in the northwest, more like the trajectories of 15 May. The transition height between these two types of trajectories was about 1200 m or 880 mb (289–290 °K). Trajectories terminating higher than about 800 m (925 mb) on 17 May also descended through about 200 mb and had four-day origins over the Bering Sea. The back trajectories from 19 and 20 May were directly from the north suggesting that the air masses sampled had had some continental influence, although there was more than 200 mb of subsidence in these trajectories enroute to the study site.

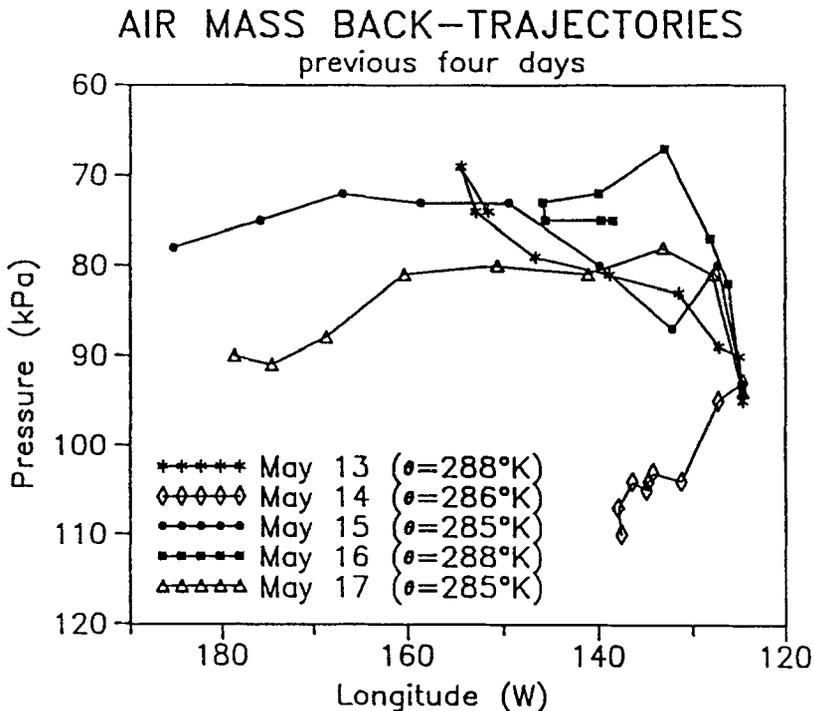


Fig. 4. The vertical motion (in pressure height) of the isentropic back-trajectories for 13–17 May 1987 at 1700 local time (Figure 3). The symbols are at 12 hour intervals. Most of the trajectories show subsidence near the coast. The trajectory for May 14 was calculated using surface winds and was apparently within the boundary layer during the entire four days.

4. Seawater DMS Distributions

April/May is the transition period in the temperate latitudes between 'winter' seawater DMS values of approximately 0.7 nmol/L and 'summer' concentrations of approximately 2.2 nmol/L (Bates *et al.*, 1987). DMS concentrations on the continental shelf can be much higher and more variable, and are strongly dependent upon the amount of coastal upwelling. This coastal upwelling occurs during westerly to northerly winds as a result of Coriolis forcing. Average DMS concentrations along the Washington coast (46–49° N) are summarized in Table I.

Sampling transects were run from Portage Head (Figure 1) upwind. The concentrations measured on the transect during June 1986 were typical of upwelling conditions along the coast. The upwelling was clearly evident by the low surface seawater temperatures. The cold (approximately 9 °C) nutrient (nitrate) rich water was high in CO₂ (low pH) and low in chlorophyll and DMS (Figure 5). As the water moved offshore, the nutrients were quickly consumed by the phytoplankton with a resulting decrease in CO₂ (increase in pH) and an increase in chlorophyll and seawater DMS concentrations (Figure 5). A similar peak in DMS concentrations was observed during the senescence phase of planktonic blooms in seawater tanks (Nguyen *et al.*, 1988).

During 11–15 May 1987, the passing cold fronts with their southerly winds brought a halt to the coastal upwelling. Surface seawater temperatures on the continental shelf were uniformly 12 °C while chlorophyll concentrations were highest near-shore. DMS concentrations were also high near-shore (Figure 6 and transect 87-1; 14.4–15.4 May in Figure 1). Transect 87-2 (16.4–17.2 May) followed the Vancouver Island coastline (Figure 1) and transited patches of high nutrients, chlorophyll and DMS concentrations. The concentrations of these parameters showed no apparent correlations. The strong westerly winds that began during the afternoon of 16 May initiated the return of the coastal up-

Table I. Coastal seawater DMS concentrations (nmol/L)

Cruise	Near-shore <100 km			Off-shore >100 km		
	Mean	Std. dev.	<i>n</i>	Mean	Std. dev.	<i>n</i>
May 1983 ^a	1.9	0.8	12	1.0	0.3	42
Feb 1984 ^a	0.6	0.1	6	–	–	–
Aug 1984 ^a	2.6	1.1	3	–	–	–
May 1985 ^b	2.2	0.6	33	0.8	0.2	4
April 1986	4.1	1.8	32	2.0	0.7	25
June 1986	4.3	2.7	27	–	–	–
May 1987	5.1	2.7	77	2.2	0.3	3

^a Bates and Cline (1985),

^b Andreae *et al.* (1988).

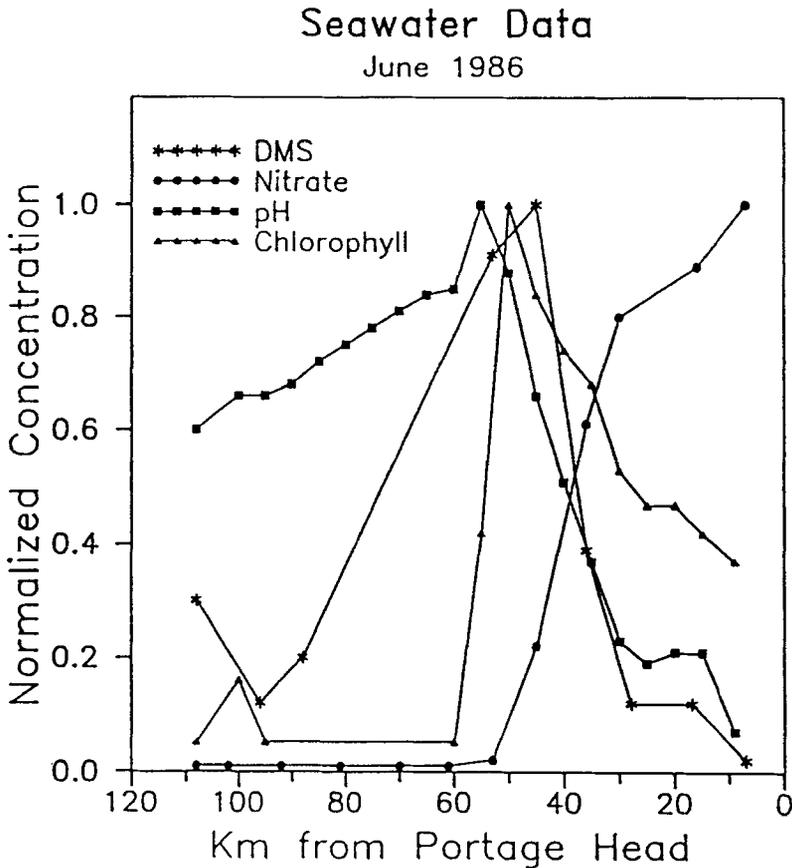


Fig. 5. Surface seawater temperature, chlorophyll *a*, pH, nitrate and DMS along transect 86 (Figure 1) taken during 13 June 1986. The concentrations have been normalized to the highest value measured on the transect.

welling. By 0800 on 17 May, surface seawater temperatures 25 km from Portage Head had dropped to 10.5 °C and by 1400 the temperature had dropped to 9 °C. This upwelling continued through the end of the cruise. DMS concentrations (Figure 6) during the upwelling period (Transect 87-3; 19.5–21.3 May) were similar to 13.1–13.7 June 1986 (Figure 5) with low values in the colder upwelled water and a concentration maximum approximately 50 km from shore.

5. Atmospheric DMS Measurements

Atmospheric DMS measurements were made concurrently aboard ship and on shore. The atmospheric data have been divided into three periods corresponding to the different meteorological conditions. Period 1, 14 and 15 May (Figure 7), was dominated by a post-frontal westerly flow during which time the boundary-

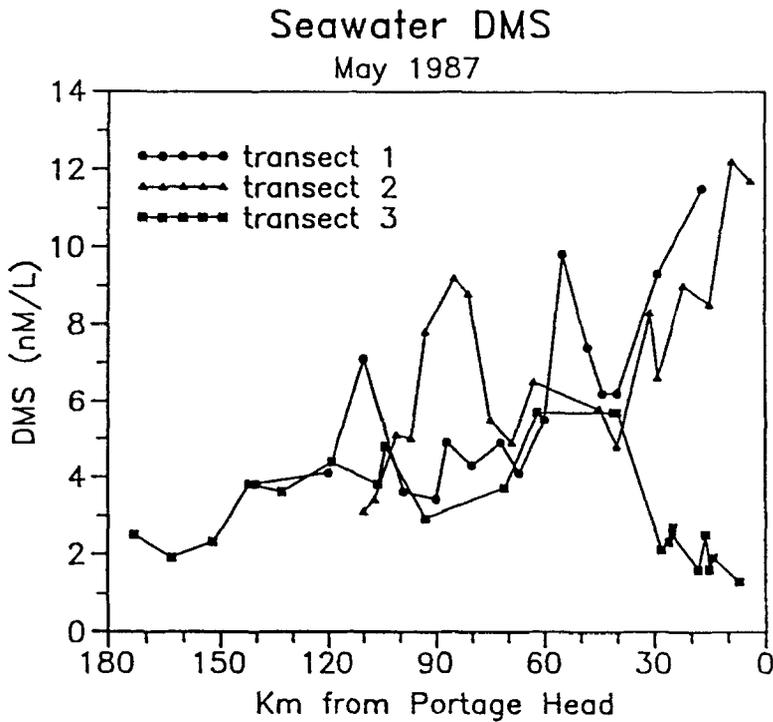


Fig. 6. Surface seawater DMS concentrations (nmol/L) during May 1987. Transect 1 (14.4–15.4 May); transect 2 (16.4–17.2 May); transect 3 (19.5–21.3 May). Transect locations are shown in Figure 1. Coastal upwelling during transect 3 resulted in low DMS concentrations near-shore.

Table II. Average wind data (m/s) (12 hour averages ending at times listed)

Date	Time	Trajectory wind	Ship wind	Cheeka Peak wind
13	1700	6.2	7.9 ± 1.2	
14	0500	–	10.8 ± 5.1	
14	1700	6.5	4.8 ± 1.5	2.8 ± 0.7 ^a
15	0500	–	6.2 ± 0.8	2.1 ± 0.5
15	1700	4.6	5.9 ± 1.8	3.2 ± 1.2
16	0500	–	4.9 ± 2.5	
16	1700	3.8	7.5 ± 6.2	3.8 ± 2.1 ^a
17	0500	–	16.4 ± 2.1	
17	1700	6.7	10.5 ± 1.9	4.1 ± 1.0
18	0500	–	18.3 ± 2.8	
18	1700	–	16.6 ± 1.9	
19	0500	–	7.3 ± 4.7	
19	1700	5.0	3.9 ± 2.3	
20	0500	–	2.5 ± 1.8	
20	1700	4.0	3.9 ± 3.2	

^a averaged from 0900–1700.

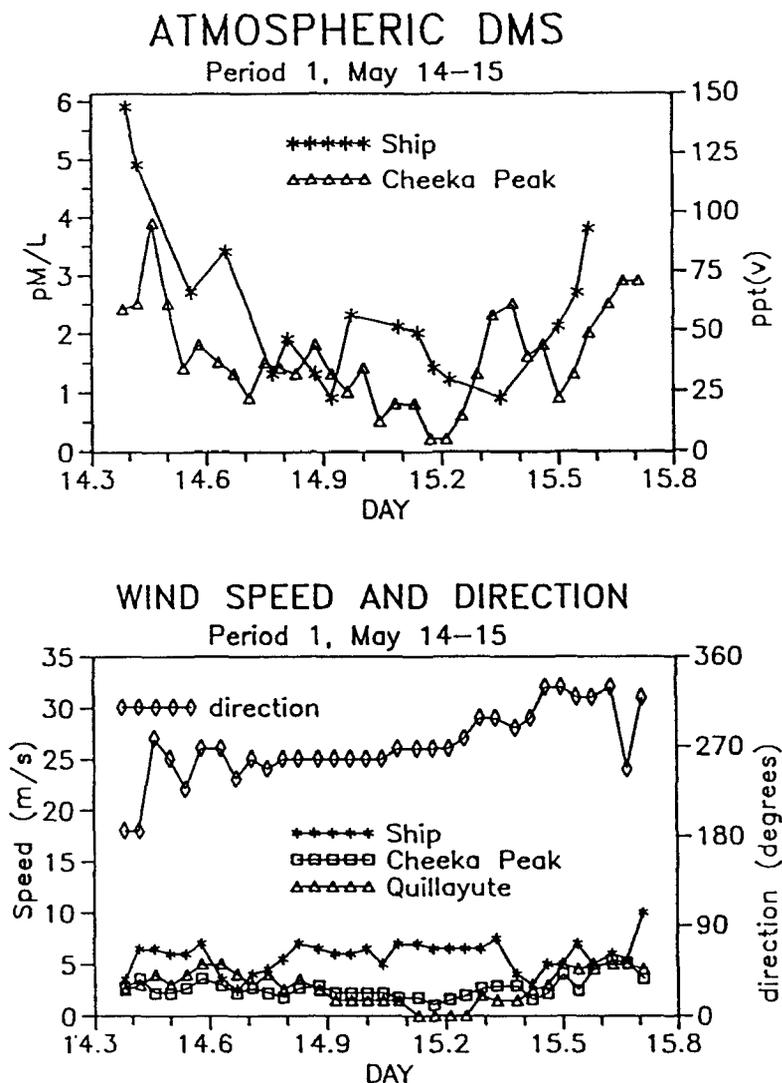


Fig. 7. Wind (m/s) and atmospheric DMS (pmol/L) data from period 1, 14–15 May 1987. DMS measurements were made both onboard ship and at Cheeka Peak. Wind speed was recorded on the ship, peak, and at the National Weather Service's station at Quillayute. The wind direction data (expressed in degrees) were taken from the ship's records.

layer height was approximately 1.7 km (Figure 2). Winds during the previous 12 hours averaged 10.8 m/s at the ship and decreased during period 1 to an average of 5.6 m/s (Table II). DMS concentrations initially decreased, perhaps as a result of the decreasing wind speed and, hence, decreasing air-sea exchange. Concentrations measured on Cheeka Peak were comparable with those measured onboard the McArthur except during the early morning of 15 May when the winds onshore dropped to <1.1 m/s with a corresponding decrease in DMS

(Figure 7). The post-frontal meteorological conditions during period 1 were similar to the periods sampled by Andreae *et al.* (1988) during May 1985. The column integrated DMS concentration during period 1, 1987 ($2.9 \mu\text{mol}/\text{m}^2$), assuming a constant concentration in the mixed layer, was approximately a factor of 3 higher than that measured in 1985. Correspondingly, the average seawater DMS concentrations were also a factor of 3 higher in 1987 than in 1985 (Table I).

Period 2, 16 and 17 May, was dominated by a stationary high pressure center

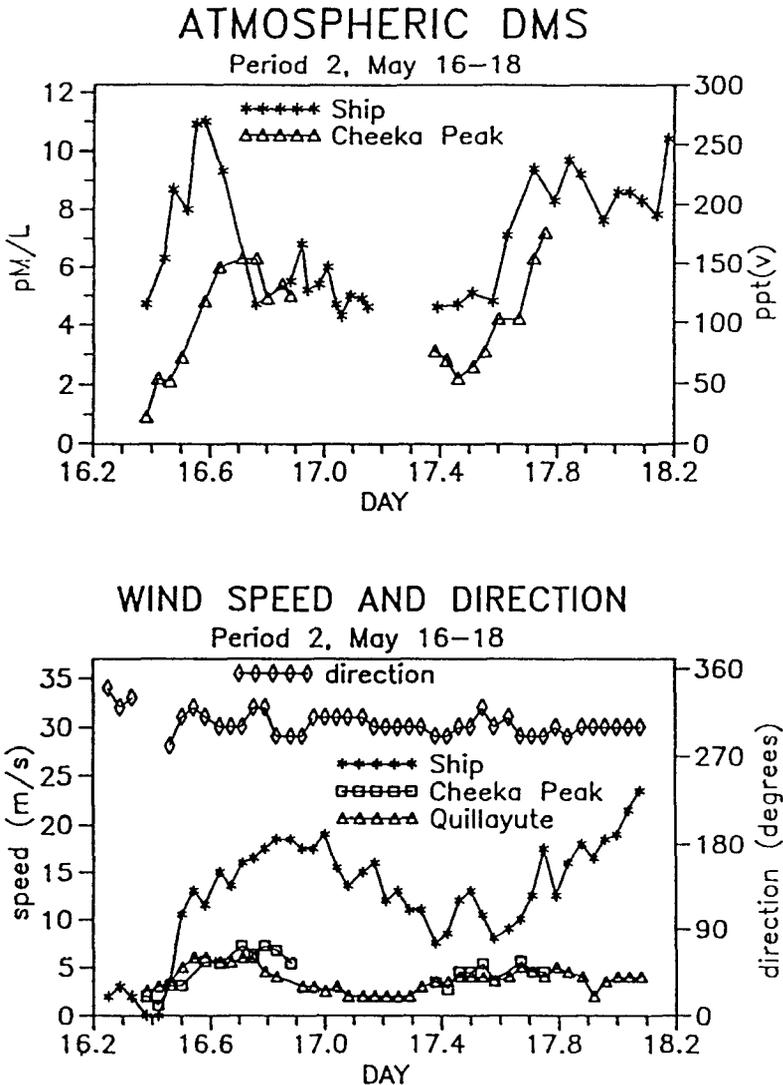


Fig. 8. Wind and atmospheric DMS data from period 2, 16–18 May 1987. See Figure 7 for additional details.

to the west with westerly flow over the study area (Figure 8). During the morning of 16 May, a period of low boundary-layer height (0.4 km) and low wind speed, atmospheric DMS concentrations measured on the ship (near the DMS source) were approximately a factor of 3 higher than those measured on the peak (Figure 8). As the wind speed and boundary-layer height rapidly increased during the late morning, the DMS concentrations measured on the ship and peak increased, finally converging later in the day (Figure 8). A similar, but less dramatic episode occurred during the morning of 17 May although the wind speed measured at the sea surface never dropped below 5 m/s. Overall, DMS concentrations measured during period 2 were higher than during period 1, presumably as a result of the lower boundary-layer height during period 2. There was no indication of a diurnal variation in the atmospheric DMS concentration as a result of photo-oxidation (Andreae *et al.*, 1985; Berresheim, 1987) although the expected variations (factor of 0.3, Andreae *et al.*, 1985) would have been negligible compared to the effects of large changes in boundary-layer heights and wind speeds. The average wind speed of the air parcel, calculated from its 12 hour back trajectory (Table II), increased from 3.8 m/s between 0500 and 1700 on 16 May to 6.7 m/s between 0500 and 1700 on 17 May, which theoretically (Smethie *et al.*, 1985) would increase the flux of DMS to the atmosphere. This may explain the sharp increase in atmospheric DMS concentrations measured both on the ship and at the peak toward the end of 17 May (Figure 8).

Period 3, 19–20 May, was characterized by an extremely low boundary-layer height (approximately 0.3 km, Figure 2) and light and variable winds (Figure 9). DMS concentrations measured on board ship during this period were extremely variable (Figure 9). At this point the shore based measurements had moved from the Peak to the beach immediately west of the Peak. The concentrations measured at the beach were more uniform, but decreased rapidly when the winds dropped to near zero (Figure 9). The sharp decrease in concentration would imply a DMS lifetime of less than 4 hours. Local concentrations of IO (Chameides and Davis, 1980; Martin *et al.*, 1988) or NO_x (Tyndall *et al.*, 1986; Atkinson *et al.*, 1984) may have been sufficient to degrade DMS this rapidly since the air mass had been over the North American continent during the previous four days (see Section 3). An alternative explanation, however, is that the easterly component of the wind, which preceded the zero wind speed (Figure 9), advected air with no DMS to the beach. Nevertheless, an important conclusion that can be drawn from this period is that the beach and surf zone were not a major source of DMS to the atmosphere.

Although the ship was crossing regions of different seawater DMS concentrations (Figure 6), there was no apparent correlation between the varying seawater and atmospheric DMS concentrations. The periods of high variability in atmospheric DMS concentrations (see Figure 9) appeared to be mainly a function of the low wind speeds and, hence, the incomplete mixing of DMS through

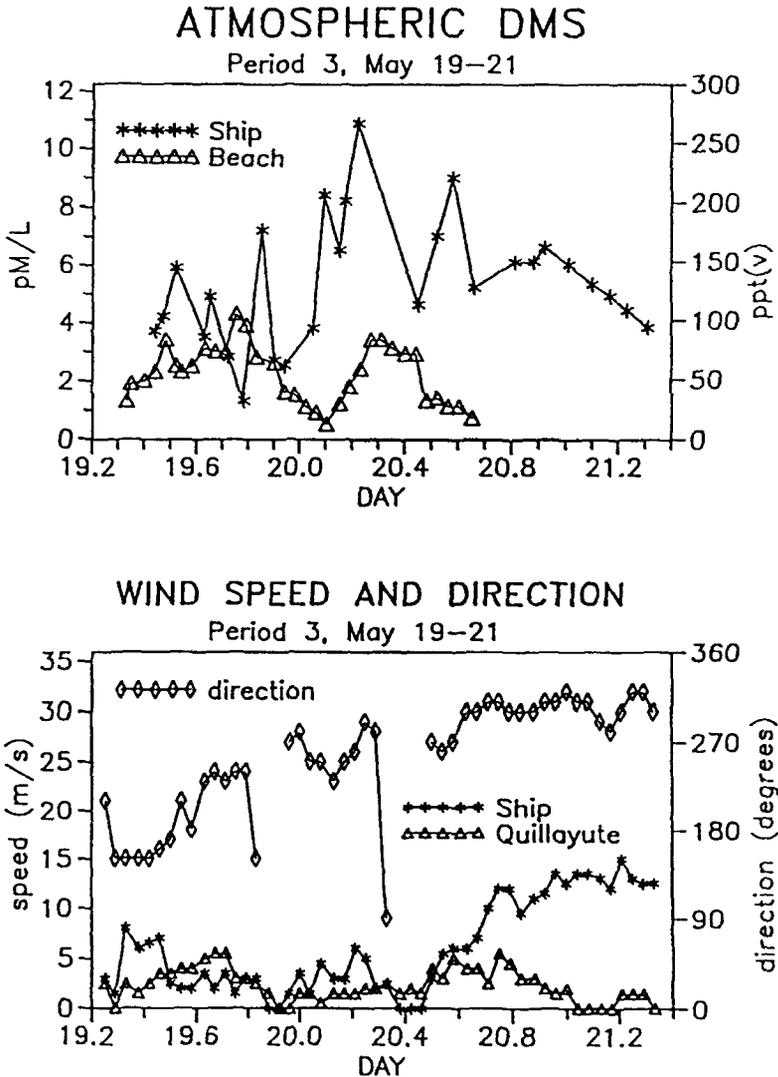


Fig. 9. Wind and atmospheric DMS data from period 3, 19–21 May 1987. DMS measurements were made on the ship and on the beach immediately west of Cheeka Peak. Winds on shore were light and variable.

the boundary layer. There was also no significant difference in atmospheric DMS concentrations measured near-shore and concentrations measured off the continental shelf when the wind speeds were greater than 5 m/s. These data, along with the covarying ship and Cheeka Peak data (Figures 7 and 8), suggest that the elevated DMS concentrations in the continental shelf waters have no measurable effect on the regional atmospheric DMS concentration. Box model calculations suggest that the high DMS concentrations on the continental shelf

could increase the concentration of atmospheric DMS measured on shore by 50% (see Section 8). Such an increase would be difficult to detect given the high variability in the measured concentrations (Figures 7–9).

6. Atmospheric SO₂ Measurements

The gas phase SO₂ concentrations measured at Cheeka Peak averaged 5.5 ± 1.8 nmol/m³ and were correlated with aerosol NSS SO₄²⁻ concentrations ($r = 0.76$) (Figure 10). There was no apparent correlation with either DMS concentrations or boundary-layer height, although such correlations would be obscured by the long (approximately 1 day) SO₂/aerosol sampling periods. The SO₂ concentrations measured during May 1987 were appreciably higher than those measured by Andreae *et al.* (1988) in May 1985 (0.2 nmol/m³) and were also higher than average mid-ocean boundary-layer concentrations of 1–2 nmol/m³ (Bonsang *et al.*, 1980; Nguyen *et al.*, 1983). Although we can not rule out local contamination, the air mass trajectories, low field blank values (Section 2), and strong correlation with NSS SO₄²⁻ support the integrity of the data. Unfortunately we had no means of measuring the input of SO₂ from the free troposphere.

7. Atmospheric Aerosol Measurements

Aerosol MSA concentrations averaged 0.32 ± 0.13 nmol/m³ on the ship (range 0.23–0.62 nmol/m³) and 0.22 ± 0.06 nmol/m³ at Cheeka Peak (range 0.16–0.32 nmol/m³). There was no apparent correlation of MSA with any chemical (DMS, SO₂, NSS SO₄²⁻) or meteorological (boundary-layer height, wind speed and direction, incident solar radiation) parameter. Again, such correlations would be obscured by the long SO₂/aerosol sampling times (Section 6).

MSA concentrations exhibit a pronounced seasonal cycle in temperate latitudes (Saltzman *et al.*, 1986; Ayers *et al.*, 1986; Watts *et al.*, 1987), similar to the seasonal cycle of DMS (Bates *et al.*, 1987; Turner *et al.*, 1988). MSA concentrations measured along the Washington coast during May 1987 were remarkably similar to May of 1985 (0.2–0.3 nmol/m³, Andreae *et al.*, 1988) and were only slightly higher than typical winter values at this latitude (0.15 nmol/m³ in winter vs. 1.8 nmol/m³ in summer; Saltzman *et al.*, 1986). The low MSA values in May 1985 were consistent with the concurrent low DMS concentrations (Andreae *et al.*, 1988). However, DMS values in May 1987 were much higher (Sections 4 and 5) and were characteristic of summer concentrations (Bates *et al.*, 1987). A possible reason for this imbalance is an enhanced production of SO₂ vs. MSA from the oxidation of DMS during May of 1987. Berresheim (1987) recently found the opposite enhancement in the Antarctic atmosphere which he attributed to the cold high latitude temperatures. Unfortunately, the parameters affecting the relative proportions of the various DMS oxidation products are not adequately known to resolve these imbalances.

Although less pronounced, NSS SO_4^{2-} concentrations show a seasonal cycle similar to that of MSA and DMS (Saltzman *et al.*, 1986). This seasonal cycle is not always evident since the signal is often complicated by continental/anthropogenic sulfate or sea salt sulfate (Prospero *et al.*, 1985). The latter problem was overcome in this study by using a cyclone separator to eliminate the majority of the sea salt (see Section 2). The measured aerosol NSS SO_4^{2-} concentrations during May of 1987 averaged $5.3 \pm 2.5 \text{ nmol/m}^3$ on the ship and $5.1 \pm 1.9 \text{ nmol/m}^3$ at Cheeka Peak. Although the sampling start and stop times at the two sites were not coincident, the data appear to track each other (Figure 10). These values are similar to those measured by Andreae *et al.* (1988) in May 1985 ($3\text{--}6 \text{ nmol/m}^3$) and to the 'clean' values reported from Shemya (53° N , 174° E) by Prospero *et al.* (1985) (6.8 nmol/m^3). The highest NSS SO_4^{2-} concentrations (8.2 nmol/m^3 from 14.4–15.4 May and 9.1 nmol/m^3 from 17.4–19.9 May) measured aboard ship during May 1987 were during periods of highest boundary layer height (Figure 2) suggesting an input of NSS SO_4^{2-} from the free troposphere. This would be consistent with the descending air mass trajectories (Figure 4). Further evidence for a tropospheric input of NSS SO_4^{2-} was observed in the MSA/sulfate ratio (Figure 11) which was lowest when the boundary layer height was highest (Figure 2). If the highest MSA/sulfate ratios (10.4%) are representative of marine sulfur, the concentration of marine NSS SO_4^{2-} at the sea surface

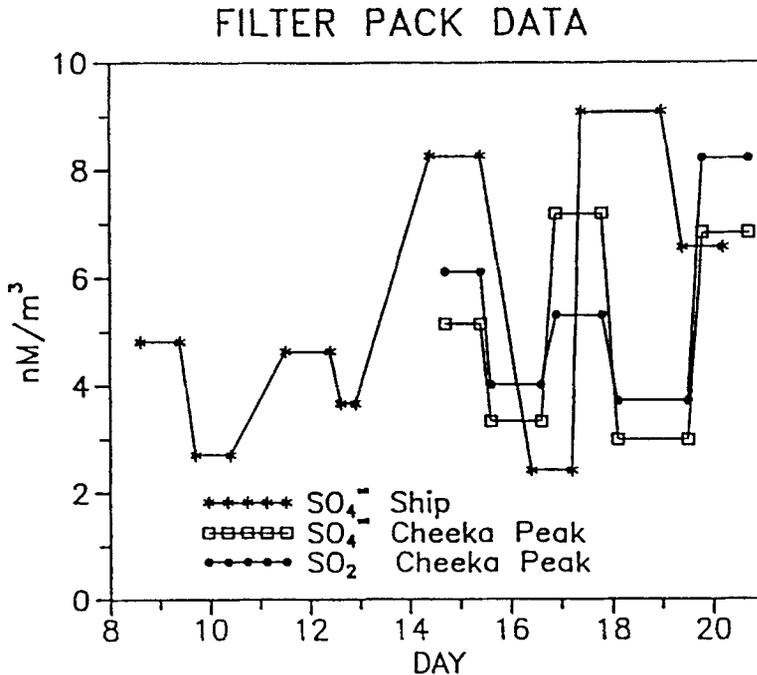


Fig. 10. Sulfur dioxide and sulfate concentrations (nmol/m^3) measured aboard ship and at Cheeka Peak during May 1987. The horizontal lines indicate the integrated sampling period.

during May 1987 would be approximately 3.1 nmol/m^3 , or roughly half the total NSS SO_4^{2-} concentration.

8. The Biogeochemical Sulfur Cycle

The sulfur species described above comprise the major components of the marine boundary layer sulfur cycle. Their concentrations and the fluxes between species should therefore be related. The data can be summarized in a simple box model (Figure 12), similar to that used by Andreae *et al.* (1986), Berresheim (1987) and Andreae *et al.* (1988). The basic assumption of such a model is that the system is in steady state. It is obvious from the rapidly changing meteorology (Section 3), the periodic inputs of sulfur from the free troposphere (Sections 5–7), and the fluctuating concentrations of the various species within the mixed layer (Sections 4 and 5), that steady state was rarely achieved. It is still instructive, however, to create an ‘average’ model for May of 1987 to evaluate the consistency of the various steps in the cycle and to compare this cycle with those mentioned above.

For the purposes of this model, we have taken an average boundary layer height of 1 km. We assume that the marine boundary layer was vertically well mixed (and therefore omit the high atmospheric DMS values at low wind

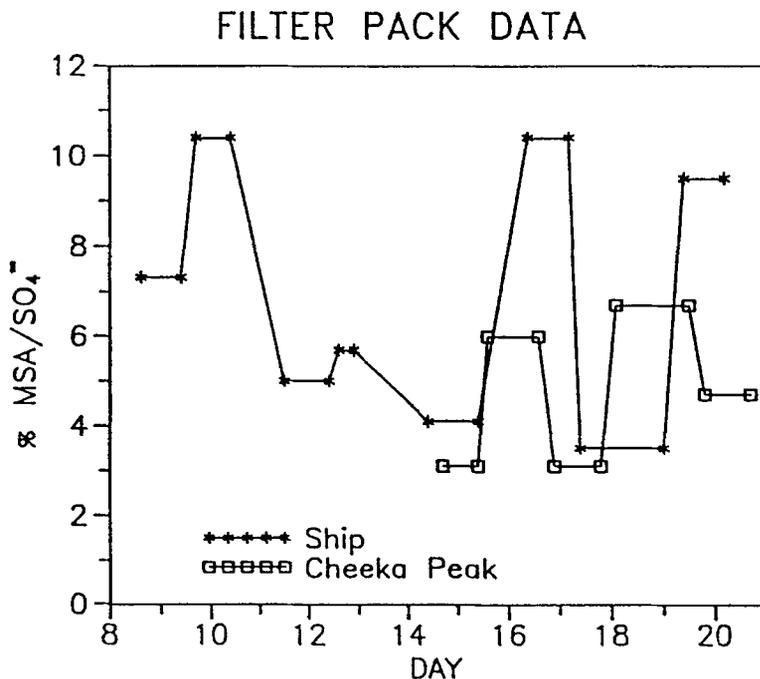


Fig. 11. Percent ratio of methane sulfonate to sulfate measured aboard ship and at Cheeka Peak during May 1987. The horizontal lines indicate the integrated sampling period.

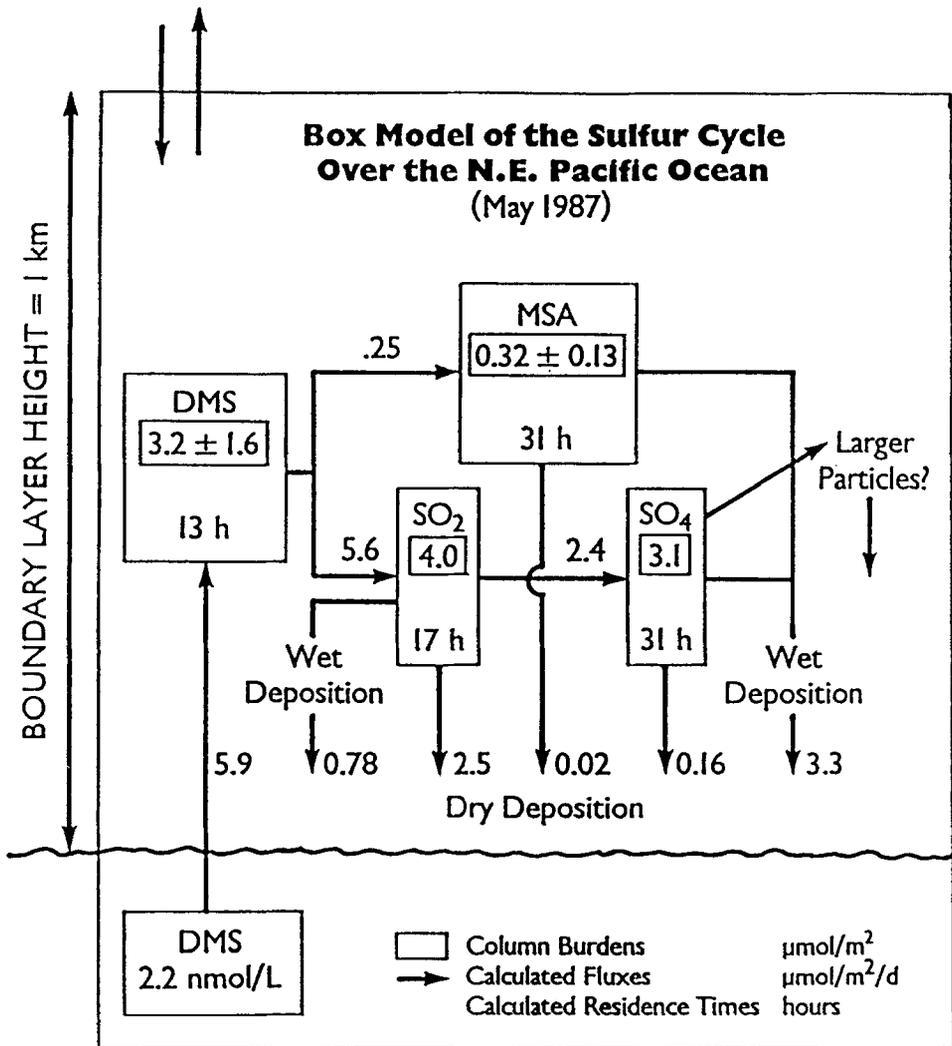


Fig. 12. Box model of the biogeochemical sulfur cycle over the northeast Pacific Ocean during May of 1987. The fluxes and inventories are best estimates, and have not been forced to balance. The model uses an average boundary layer height of 1 km and measured concentrations of seawater DMS, atmospheric DMS and aerosol MSA. The concentrations of atmospheric SO₂ and aerosol SO₄²⁻ are calculated from the MSA concentration (see text). The calculated flux of DMS from the ocean to the atmosphere is propagated through the model with an SO₂/MSA branching ratio based on equal residence times for MSA and SO₄²⁻. The wet deposition of SO₂ is calculated from the equilibrium solubility, while the wet deposition of SO₄²⁻ is determined from measured concentrations. The dry depositions are calculated from dry deposition velocities. The residence times are calculated based on the concentrations and fluxes.

speeds), that the net horizontal transport was zero, and that the only exchange with the free troposphere was the periodic addition of SO₂ and SO₄²⁻. The subsiding air masses (Figure 4) and resulting atmospheric stability likely confined the DMS and MSA to the mixed layer (Andreae *et al.*, 1988).

The flux of DMS into this box was calculated from gas exchange models (Liss, 1973) which use the concentration of DMS in seawater and an exchange coefficient dependent upon wind speed (Smethie *et al.*, 1985). Based on an average seawater temperature of 11 °C and an average wind speed measured aboard ship of 8.5 m/s (Table II), the calculated DMS exchange coefficient was 2.7 m/d (Bates *et al.*, 1987). Since the high seawater DMS concentrations on the continental shelf had no measurable effect on the atmospheric concentration of DMS (Section 5), we have used the average open ocean DMS concentration (2.2 $\mu\text{mol/L}$) combined with the DMS exchange coefficient (2.7 m/d) to calculate an ocean-atmosphere DMS flux of 5.9 $\mu\text{mol/m}^2/\text{d}$ (Figure 12).

The column burden of DMS was determined for each period (Section 5), assuming a uniform DMS concentration throughout the boundary layer, and averaged to obtain a column integrated concentration of $3.2 \pm 1.6 \mu\text{mol/m}^2$. This burden, along with the air-sea exchange parameters discussed above, can be used to calculate the effect of the high continental shelf DMS concentrations on the atmospheric sulfur cycle. Assuming an average DMS concentration in the surface waters of the continental shelf of 6 nmol/L (Figure 6) and an average shelf width of 100 km, the added input of DMS to the atmosphere would be $(6-2.2 \text{ nmol/L}) (2.7 \text{ m/d}) (100 \text{ km}) = 1.0 \text{ moles/m of coastline/d}$. This compares to an input flux from the open ocean of $(3.2 \mu\text{mol/m}^2) (8.5 \text{ m/s}) = 2.4 \text{ moles/m of coastline/d}$. The calculated effect of the continental shelf DMS concentrations, therefore, would be an increase in the atmospheric DMS concentration at the coast of approximately 50%. This increase is well within the natural variability of the measured concentrations (Figures 7–9).

The calculated atmospheric DMS residence time based on the column burden and ocean-atmosphere flux was 13 hours. This was considerably less than that calculated for the Antarctic atmosphere by Berresheim (1987), although the atmospheric sulfur chemistry in this polar region was unusual in that the concentration of MSA was nearly equal to the concentration of SO_4^{2-} . A 13 hour DMS residence time is also less than that predicted from the reaction of DMS with the OH radical. Assuming an OH concentration of $10^6 \text{ molecules/cm}^3$ and rate constant of $6.3 \times 10^{-12} \text{ cm}^3/\text{molecule/s}$ (Atkinson, 1986), the loss of DMS from the atmosphere would be 1.7 $\mu\text{mol/m}^2/\text{d}$ (Figure 12) giving a DMS residence time of approximately 2 days. Lower residence times would be possible if the concentration of IO (Martin *et al.*, 1988) or NO_x (Andreae *et al.*, 1985) was sufficiently high. Given the uncertainties in the reactions of atmospheric DMS, we have based the fluxes between species in this model on the air-sea exchange of DMS (Figure 12).

The average concentration of MSA measured on the ship was $0.32 \pm 0.13 \text{ nmol/m}^3$. Assuming an MSA/ SO_4^{2-} ratio of 0.10 (Section 7) for the marine derived SO_4 , the average atmospheric burden of marine SO_4^{2-} was 3.1 $\mu\text{mol/m}^2$. This calculation presumably excludes the SO_4^{2-} input flux from the free troposphere. Similarly, since the SO_2 and SO_4^{2-} concentrations at Cheeka Peak were

correlated (Section 6), the SO_4^{2-} concentration can be used to calculate the $4.0 \mu\text{mol}/\text{m}^2$ boundary-layer SO_2 burden shown in Figure 12. Again, this calculation presumably subtracts out the SO_2 derived from the free troposphere. Since MSA and SO_4^{2-} were both present on sub- μm particles, they should have had similar residence times. Using this constraint, the input fluxes of MSA and SO_2 were calculated to be 0.25 and $5.6 \mu\text{mol}/\text{m}^2/\text{d}$, respectively. The input flux of SO_4^{2-} from SO_2 was calculated by difference between the SO_2 input flux and the SO_2 dry and wet deposition (discussed below). This flux ($2.4 \mu\text{mol}/\text{m}^2/\text{d}$, Figure 12) is approximately a factor of 10 higher than the calculated homogeneous gas phase oxidation of SO_2 (using 10^6 molecules of OH/cm^3 and a rate constant of $1.1 \times 10^{-12} \text{ cm}^3/\text{s}$), supporting the importance of liquid-phase oxidation of SO_2 (Hegg, 1985).

The calculated boundary-layer residence times for SO_2 and the MSA and SO_4^{2-} aerosols were 17 and 31 hours, respectively. The SO_2 residence time was in good agreement with an average of many studies (15 ± 3 hours) calculated and summarized by Bonsang *et al.* (1987). The aerosol lifetime was similar to that calculated by Quinn *et al.* (1988) for NH_4^+ (22 hours) during the same study and that calculated by Vong *et al.* (1988) for SO_4^{2-} (48 hours) in the same region during April/May 1984. A 31 hour residence time was considerably less than that used by Andreae *et al.* (1988) for May 1985 (3.5 d). This longer residence time was likely representative of SO_4^{2-} in the free troposphere (Whelpdale *et al.*, 1988).

The dry deposition of the various species was calculated using deposition velocities of $600 \text{ m}/\text{d}$ for SO_2 and $50 \text{ m}/\text{d}$ for MSA and SO_4^{2-} aerosol particles (Galloway, 1985). The wet deposition of SO_2 and SO_4^{2-} were calculated based on the rain measured during the frontal passages of 12 and 14 May. The average SO_4^{2-} concentration was $1.7 \text{ nmol}/\text{ml}$ (range of 1.2 – $2.2 \text{ nmol}/\text{ml}$) in a total of 27 mm of rainfall. This total deposition, averaged over the 14 days of the study, amounted to a flux of $3.3 \mu\text{mol}/\text{m}^2/\text{d}$. The concentration of SO_2 in rainwater, calculated both from the equilibrium solubility (Charlson *et al.*, 1983) and from washout ratios (Davies, 1984) was $0.4 \text{ nmol}/\text{ml}$. This concentration, combined with the 27 mm of rainfall over 14 days, gave a flux of $0.78 \mu\text{mol}/\text{m}^2/\text{d}$. Within the errors of the measurements, the downward flux of sulfur ($6.8 \mu\text{mol}/\text{m}^2/\text{d}$) matched the oceanic DMS flux ($5.9 \mu\text{mol}/\text{m}^2/\text{d}$) (Figure 12). Furthermore, based on calculated residence times and fluxes, excluding the input of sulfur from the free troposphere, the concentrations and fluxes of the various sulfur species were internally consistent within the boundary layer over the northeast Pacific Ocean during May 1987. A similar conclusion was reached during the period of low DMS emissions in May 1985 (Andreae *et al.*, 1988). The principal difference in the two periods was a higher sulfur flux in 1987 which resulted in a higher concentration of SO_2 and a more rapid cycling of sulfur through the boundary layer.

9. Summary and Conclusions

The concentration of seawater DMS on the continental shelf was strongly influenced by coastal upwelling. Although this biologically productive region yielded high seawater DMS concentrations, the area appeared to be too small to have a measurable effect on the sulfur cycle in the marine boundary layer. The concentration of atmospheric DMS was strongly dependent upon wind speed and boundary layer height. At low wind speeds, the atmospheric DMS concentrations measured near the sea surface were significantly higher than the concentrations measured onshore.

The descending trajectories and low MSA/sulfate ratios indicated that during May of 1987, NSS SO_4^{2-} was periodically mixed down to the marine boundary layer from the free troposphere. Using MSA concentrations to estimate the NSS SO_4^{2-} and SO_2 of marine origin, the marine biogeochemical sulfur cycle was balanced by the emissions of biogenic DMS to the atmosphere.

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